Special Portland Cements.

By DR. GABRIEL A. ASHKENAZI.

THERE is a demand in the United States for special types of cement evolving a minimum of heat during hydration, since the development of heat causes a change of volume in the concrete and is favourable to the formation of cracks. To comply with these requirements, cement is manufactured whose composition differs from standard Portland cement, and is known as low-heat cement. It has a lower content of lime than standard Portland cement and an augmented proportion of iron oxide. The chemical composition, in terms of the four principal oxides, of a typical low-heat cement, such as was used in the construction of the Morris dam, is approximately:

SiO_2, 23 per cent.; CaO, 60 per cent.; Al_2O_3, 5 per cent.; Fe_2O_3, 5 per cent.

This therefore represents a Portland cement with a low hydraulic modulus (about 1·8), and an alumina/iron-oxide ratio equal to 0·64. The composition of this cement does not differ substantially from cements produced forty years ago. For instance, D. B. Butler[1] in 1888 examined an English cement with the following composition:

SiO_2, 23·4 per cent.; CaO, 60·9 per cent.; Al_2O_3, 5·85 per cent.;
Fe_2O_3, 4·65 per cent.

According to Spencer B. Newberry[2], the American brand "Saylor" made in 1897 had the principal oxides in the proportions:

SiO_2, 20·6 per cent.; CaO, 62·8 per cent.; Al_2O_3, 6·9 per cent.;
Fe_2O_3, 5·4 per cent.

In 1898 the Cement Laboratory of the City of Philadelphia[3] described as a

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[1] D. B. Butler. Portland Cement. (Ed. 1905), p. 15.
[2] Cem. and Eng. News, Nov. (1897), p. 76.
[3] *Ibid.*, Jan. (1898), p. 13.

normal cement a brand of the following composition:

SiO_2, 20·99 per cent. ; CaO, 60·75 per cent. ; Al_2O_3, 4·12 per cent. ; Fe_2O_3, 5·4 per cent.

This cement contains only 1·4 per cent. of computed tricalcium-aluminate. Inasmuch as the prevalent opinion among concrete experts to-day is that the tricalcium-aluminate appears to be the most undesirable compound in cement, owing to its high heat of hydration, the last "normal cement" mentioned may represent an ideal low-heat cement.

Test Results from the Past.

These cements, made forty years ago under manufacturing conditions which may appear incredible or odd to the chemist of a modern cement plant, showed relatively satisfactory strength. In 1897, H. P. Boordman[4] published a summary of the results of tests of Portland cements delivered on public works in the United States, according to which the tensile strength of mortar (1:3) ranged from 135 lb. to 246 lb. per square inch after 7 days, and the 28-day results were 209 lb. to 316 lb. per square inch. Considering that the tensile strengths of the standard mortar of low-heat cement used in the construction of the Morris dam were 200 lb. and 231 lb. per square inch after 7 days and 353 lb. per square inch after 28 days, we must come to the conclusion that the advent of low-heat cement does not represent a step forward. The fact that low-heat cement has been used with success for mass concrete work at the Morris and Boulder dams does not contradict this opinion. Mass construction work of smaller dimensions was accomplished forty years ago without preliminary extensive laboratory investigations and with good results. For instance, at the Crystal Spring dam, which was built during the years 1887-1890, a primitively manufactured cement was used, the requirements were simple, and, according to F. M. McMillan and M. B. Lagaard[5], the dam, after forty years, shows a concrete of hard and durable quality, without cracks or leakage, which passed uninjured through the San Francisco earthquake. It is true that standard cement, used in some places for mass concrete, did not prove quite satisfactory. For instance, the concrete of the Owyhee dam, built of standard Portland cement, developed circumferential cracks, but whether the occurrence of this extensive cracking was caused by the cement used is not proved. There is an opinion that "a change in type of cement alone would probably not have altered the behaviour of concrete greatly[6]."

It is generally agreed that cement is only one of the numerous factors which can affect the properties of concrete. Incorrect mixing, incorrect grading, excess of water and improper curing are not of less importance than the properties of the cement. It is not within the scope of this article to discuss in detail the effects of different factors on the durability of mass concrete in connection with the complicated movements in it while it is hardening. This process is very slow, and

[4] Cem. and Eng. News, Aug. (1897), p. 20.

[5] Eng. News Rec.

[6] J. L. Savage. Special Cements for Mass Concrete, p. 9.

starts with the formation of a colloidal mass of calcium hydrosilicates.   These hydrogels are characterised by their tendency to absorb a great amount of water. The interior of mass concrete dries very slowly and considerable strain may be caused by the variation of temperature due to the heat of hydration.   This is the reason why the user of mass concrete looked for a cement developing a mini- mum amount of heat.   It should be mentioned, however, that the heat of hydration plays only a subordinate role in comparison with other factors.   The gain in temperature of 10 deg. F., or even 15 deg. F., by using low-heat cement instead of Portland cement is often unimportant in comparison with the differ- ences between the initial and maximum temperatures of concrete due to the climatic conditions.   According to J. L. Savage[7] "it is apparent that the placing temperature may have a much more important bearing on the tempera- ture drop and consequent contraction of the concrete than any change that may be effected by varying the heat generating characteristics of the cement."   Inas- much as when low-heat cement is used the gain in the smaller heat development goes parallel with a considerable loss of strength, the benefit achieved is very questionable.   Practice shows that low-heat cement, due to its low early strength and slow rate of hardening, cannot be used during the cold months, and in the construction of the Boulder dam the low-heat cement was mixed with standard cement in order not to handicap construction during the winter.   The lowest mean minimum monthly temperature at the site of the dam is 39 deg. F. only.

Cement which is to be used in mass concrete should be capable of hardening at low temperatures and should evolve most of its heat of hydration within the first days; it should also produce a concrete having sufficient tensile strength to withstand cracking during cooling.   Low-heat cement does not comply with these requirements.   Its heat of hydration is developed slowly at early ages, and the development persists for a long time, whereas standard Portland cement generates its heat of hydration during the first days.   The small strength of low- heat cement in the first few days and the slow gain in strength are disadvan- tageous for construction at low temperatures.   It is true, as engineers frequently point out, that the compressive strength of cement is not very important in mass construction, since the working stresses in mass concrete are low.   Every engi- neer will agree, however, that the production of high tensile strength in order to prevent cracking is of great importance. The tensile strength of low-heat cement is particularly low, that used at the Morris dam being a typical example.   The results of laboratory tests on standard mortar give only an approximate idea of the strength which may be developed in concrete.   The Engineering Materials Laboratory of the University of California[8] examined the tensile strength of specimens (6-in. by 33-in. cylinders) made of low-heat cement, similar to one used in the construction of the Boulder dam.   The cement content was one barrel per cubic yard of concrete; the water-cement ratio was 0·40, and the

[7] J. L. Savage.   Special Cements for Mass Concrete, p. 3.
[8] R. E. Davis.   Use of Portland Puzzolan Cement for Bonnevile Dam in "Special Cements for Mass Concrete," p. 159?

aggregates were from ·1½ in. downwards.   The specimens were cured under special conditions in sealed containers, under temperature conditions simulating those which would occur in mass concrete containing the particular cement, having the particular cement content, and cast at 40 deg. F. (mass-concrete curing).   After five days the specimens showed a tensile strength of 40 lb. per square inch, an exceptionally poor result.   The fact that these specimens showed a tensile strength of 225 lb. per square inch after 28 days, and at 90 days 285 lb. per square inch, is no evidence that the same gain in strengths will be produced in big blocks of concrete subject to alternate shrinkage and expansion which differ essentially from the movements in the small specimens.   As a rule, the tensile strength of mass concrete is considerably lower than that found by testing in the laboratory specimens made of the same mixture.   Considering the small size of the aggregates and the high water-cement ratio, it can be assumed that the tensile strengths of mass concrete in the given case will not reach even the small figures mentioned.

Modified Portland Cements.

The process of hardening of cement is associated with the formation of hydrogels which tend to absorb a great quantity of water.   This amount, however, is limited.   On the other hand, it is known that the finest particle of cement is, after a long period of time, not completely hydrated.   The modern practice in mass concrete work is to use a lean mix with a comparatively large amount of mixing water.   Inasmuch as only a small part of the cement grain is hydrated and the hydrogel is saturated with chemically bound and absorbed water, free water exists in the mass of concrete.   The lower the early strength of the cement. the slower the rate of hardening, the less is the quantity of gel formed and the less the amount of fixed water.   Consequently more free water will be present in the concrete.   The low-heat cement with its slow hardening properties favours the formation of free water in concrete.   It is well known what serious effects this water may have, especially in mass concrete.   There is little doubt that the advantage which can be derived from the use of low-heat cement is very slight in comparison with its other inconvenient properties.   It may be for this reason that, in the latest mass concrete work, another type of Portland cement has been used, the so-called "modified Portland cement."   The specification for this type of cement, which is selected for the construction of the Grand Coulee dam, restricts its theoretical compound composition to:

Tricalcium silicate—not less than 35 per cent., not more than 55 per cent.
Tricalcium aluminate—not more than 7 per cent.

In respect to the computed amount of C_3A, this type belongs to the same category as the low-heat cement, and in respect to the content of computed lime-silica compounds it does not differ from standard Portland cement, thus representing a mean between these two binding materials.   It develops sufficient strength to permit early form removal and manipulation at lower placing temperature, and generates a moderate heat of hydration ranging to about 80 cal./g. at seven days.   Its early tensile strengths are higher than those of low-heat

cement, but are inferior to those of good Portland cement.   For instance, the tensile strength of concrete made of 0 to $1 \cdot 5$-in. aggregate with a cement content of one barrel per cubic yard and a water-cement ratio of $0 \cdot 40$ by weight, when tested on 6-in. by 33-in. cylinders cured for 5, 28 and 90 days, were 105, 265 and 295 lb. per square inch respectively.   These are quite moderate results.

Relation Between Composition and Characteristics of Cement.

Cement experts in the United States are inclined to deduce the characteristics of cement from their chemical compositions, using as a base R. H. Bogue's method of calculation of the four cement compounds.   It is well known, indeed, that the artificially prepared tricalcium-aluminate evolves by complete hydration nearly twice as much heat as each of the other artificially prepared compounds, the presence of which in cement is generally admitted.   Assuming the alumina compounds of raw materials combine with lime to form $3CaO.Al_2O_3$, and that this compound exists in commercial cement as a separate crystalline material, thus augmenting the heat of hydration, the usual way of regulating the heat of hydration of cement hinges on the limitation of the proportion of C_3A. Inasmuch as the content of alumina in the raw mix cannot be directly reduced, the proportion of C_3A in cement can be decreased by increasing the content of iron oxide in the raw mixture.   The additional iron oxide combines with lime and alumina forming tetra-calcium-alumina-ferrite, thus eliminating the binary calcium compound of alumina.   It should be mentioned, however, that there are still some doubts regarding the presence of C_3A as a separate crystalline material in commercial Portland cement.

Microscopic detection of tricalcium-aluminate in laboratory prepared combinations does not entail any difficulties.   This compound crystallises easily and rapidly and tends to form in large units.   Everyone, however, who has worked on petrographic examinations of cement clinker, knows how difficult it is to detect C_3A.   Even in cases when, according to the familiar assumptions, the amount of C_3A should be sufficient to be experimentally established, it is often impossible to detect it in commercial Portland cement.   The various explanations of this phenomenon can be reduced to the view that C_3A, crystallising in large units, encloses C_3S and CaO, thus becoming an embedment of interstitial material. Inasmuch as the optical properties of C_3A are very close to those of C_3S, and the proportion of C_3A is small in comparison with the amount of C_3S, a distinct idea cannot be obtained.   Due to the fact that C_3A controls the orientation of C_4AF crystals, its presence can be demonstrated indirectly.   According to Levi S. Brown[9] in recently published studies on tricalcium-aluminate, the structural evidences of crystalline C_3A in cement to be sought are principally two, viz., (1) large clear tubes of C_3A enclosing C_3S and possibly CaO, and (2) extended areas in which C_4AF crystals possess a common orientation exhibited as mass bi-refringence.

Brown examined, among numerous samples, three brands of cement of the following composition :—

[9] A.S.T.M. Proc. Vol. 37, part 2, pp. 277-305.

	A	B	C	
SiO_2	19.32	21.56	19.92	per cent.
CaO	65.69	66.37	67.67	,, ,,
Al_2O_3	7.02	4.25	7.17	,, ,,
Fe_2O_3	2.78	3.69	3.67	,, ,,
MgO	3.31	3.20	0.90	,, ,,

The result of petrographic examination of these cements which, according to their computed compound composition, should show distinct presence of tri-calcium-aluminate, is negative.   No cubes and no mass bi-refringence were exhibited.

Irrespective of the assumption concerning the form in which alumina may exist in commercial cement, the writer does not share the opinion of those who are inclined to see in this compound an undesirable or even dangerous element.   In his opinion the presence of calcium-alumina compounds in cement is essential in the production of early strengths.   He also thinks that the partial elimination of the binary alumina compounds, such as has been accomplished in cases of low-heat and modified Portland cement, cannot be justified by the results achieved.

The writer is aware of large-scale experiments in Europe and Japan on the production of cement completely free from binary calcium compounds of alumina and iron.   This type of cement was introduced by Professor F. Ferrari[10] in the early twenties.   Its main characteristic is the content of alumina and iron oxide in equimolecular proportions.   In many countries the manufacturers started to produce this cement, but for different reasons its production was suspended. Lately a renewed interest in Ferrari cement has been noticed.   In 1937 Dr. H. Albert[11] published an exhaustive investigation on this type of cement.   The results are remarkable, and, according to Dr. Albert, comparison of this cement with Portland cements showed its superiority in all properties.   The best results were shown by a Ferrari cement composed of 75 per cent. of C_3S and 25 per cent. of C_4AF, with a silica modulus equal to $1 \cdot 47$.   It is not intended to discuss the type of binding material at length now, since it belongs to an entirely different category from the American low-heat and modified Portland cements.   The writer is not yet inclined to generalise on the results of the recent studies on Ferrari cement, because he is cognizant of experiments with less favourable results.   As almost always occurs, the specific manufacturing conditions, especially the nature of the raw materials, play an exceedingly important part. In cases in which the admixture of iron oxide to the raw mix improves the quality of clinker, the improvement is due rather to a more exact preparation of the raw mix, which usually occurs when a small portion of an improving agent is added to the normal raw materials, and to the influence of the larger amount of sesquioxides in more perfect sintering, than to the hydraulic properties of the alumina-ferric calcium compounds.

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[10] United States Patent No. 1,372,015.
[11] H. Albert. Die Herstellung und technische Eigenschaften von Ferrari Zementen Berlin, 1937.

Accumulation of Heat in Mass Concrete.

Resuming the discussion of the American special Portland cements for use in mass concrete, the writer wishes to stress that he does not doubt the great danger of the accumulation of heat in a large mass of concrete. The danger, however, is not essentially reduced by the use of the special cements. A correctly prepared Portland cement of high early strength generates 80 to 100 calories per gram of heat of hydration at seven days. The specification requirements for the Boulder dam prescribed as a maximum 65 cal./g. The additional amount of 15 to 35 cal./g. cannot seriously affect a lean concrete such as is used in mass construction. It has been already mentioned that other factors have a much greater importance. The dangers of thermal effects on mass concrete can be diminished or even removed by improved means of dissipating the heat, namely, by using aggregates of higher conductivity, by considering in the structural design more favourable surface exposure conditions, and, especially, by the application of artificial cooling. Pipe refrigeration has been used in the construction of the Boulder dam and, according to J. L. Savage, "if artificial cooling had not been used, the ultimate maximum temperatures of the concrete would have been practically the same regardless of the type of cement used, under the same conditions and rates of placing."

The writer is of the opinion that the question of the heat of hydration of a given cement in connection with its use for mass concrete has been generally considered from a somewhat one-sided viewpoint. It is actually unimportant how many calories are generated by 1 gram of cement, but what is important is the extent of the strengths exhibited in proportion to the heat produced by 1 gram of cement. In other words, it is not the absolute rate of heat of hydration, which is fixed in the various specifications for special cements, but the strength/heat ratio that should be the criterion for estimating the qualities of cement. In this respect the modified and, still more, the low-heat cement are inefficient.

Special Requirements in Specifications.

During recent years the American cement manufacturers have been dominated by a tendency to draw a conclusion in regard to the qualities of Portland cement from its computed composition. This tendency was applied in various specifications in which the proportion of the computed compounds in cement have been limited. Two years ago the writer expressed an opinion on this subject.[12] It is sufficient to say here that the fixation of computed compounds cannot be justified; first, because our knowledge of their cumulative effect is not complete; secondly, because "no satisfactory correlations were found between the calculated composition of Portland cement clinker and its heat of hydration";[13] thirdly, because the compounds exist in cement not in the form of pure units, but partly in the state of solid solutions. C_3S tends to dissolve C_2S and C_3A; C_2F can absorb a considerable quantity of C_3A. The existence of C_4AF (Brownmillerite) in Portland cement has been confirmed by the great majority of investi-

[12] Rock Products, Sept. 1937, p. 59.
[13] H. Insley. Nat. Bureau of Stand. J. of Res., 1936 (R.P. 917). pp. 353-361.

gators.   This compound plays an important role in all specifications for the special cements of low heat of hydration.   In cement literature, however, there are indications tending to question its existence in certain cases.   Recent investigations of the constitution of celit by T. Yamaushi[14] raise new doubts regarding this compound.

Nevertheless, the tendency towards restrictions on the composition of cement, based on the calculation of the four compounds, still exists in the United States.   Lately a certain change in this tendency has been noted.   For example, P. H. Bates expresses the opinion : " We will realise more and more that we are going to improve Portland cement more by manipulation in its manufacture than by its compounds."[15]

The writer is convinced that, although the composition of Portland cement lies within certain limits, comparatively large fluctuations in the relationship of the oxides are admissible.   Strict general limitations to the content of some compounds connecting certain properties of cement with its composition are unnecessary at present.   As a consequence of the numerous specifications with similar regulations the American manufacturers have to make several kinds of cement.   The manufacture, however, must be characterised by an exactness and by a maximum of uniformity in the composition of the raw and finished products, as well as in the procedure of burning.   Such exactness is only possible in a plant which year in and year out is producing one brand of the same high quality.   It is very difficult, if not impossible, to reach this exactness if the plant is producing several kinds of cement.   Nor does the writer see any necessity for such a policy.   These remarks apply to such special types of Portland cement as the low-heat, as well as the modified cements, or other similar variants.   Blended cements, as well as blast-furnace cements, are a special domain.   Moreover, their production does not interfere with the regular course of manufacturing.

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Conclusion.

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A correctly prepared Portland cement possesses the qualities of an hydraulic binding material for the great majority of constructional purposes, mass concrete construction not excluded.   Used for the last purpose, it will produce, due to its high early compressive and tensile strengths, a lean concrete of better durability and extensibility than the special cements, whose general characteristics are an augmented proportion of iron compounds and an unsatisfactory strength—heat of hydration ratio.

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[14] Journ. Ceram. Ass., Japan.   Vol. 45, pp. 361 and 433.
[15] J. Am. Concr. Inst.   Vol. 32, 1936, p. 119

The Causes of the Bond Between Steel and Concrete.
By DR. B. POGÁNY.

THE causes of the bond between steel and concrete have been investigated for a long time, but the first important experiments, made by the commission of the French Government, were more concerned with determining the resistance at the first slip of the steel in the concrete. The resistance to slip is a dynamic value, whereas the bond is a static value, but the definitions of these, given by different authorities, are not the same. Furthermore, slip occurs at very small bending stresses, then ceases and does not reappear until the load is much greater. It then increases steadily until failure occurs. In view of these difficulties, a distinction between bond and resistance to slip is not suitable in a simple and comprehensive treatment of the stresses in reinforced concrete structures.

Early Experiments.

In the early period systematic experiments were conducted by Bach, Preuss, Probst and Schüle, and the results of these are still the basis of reinforced concrete design. These investigations can be divided into two classes according to their results.

(1) Some experimenters concluded that shrinkage was the true cause of the bond effect. C. von Bach states in *Armierter Beton*, 1910, No. 7, that the bond effect is caused by the grip which is due to shrinkage. The grip produces friction which prevents slipping. Later experiments made by Bach (together with O. Graf) show that the departure from a truly cylindrical shape and the rough surface of the steel increase the friction and allow slip to occur only when the layer of cement round the steel is destroyed by shear. According to Bach and Graf the bond is increased by a greater percentage of cement in the mortar and a greater diameter of the bar, but is decreased by a greater amount of gauging water. Schüle, who finds a definite relation between the bond, the percentage of cement and the age of the concrete, is of the same opinion and particularly stresses the importance of the percentage of cement. M. Vasilesco Karpen also states that shrinkage is the cause of the bond effect (*Comptes Rendus de l'Académie des Sciences*, Paris, Vol. XVI, p. 21) and attempts to show that the resulting pressure is a function of the moduli of elasticity of the concrete and the steel, of Poisson's ratio, and of the diameter of the bars. It seems, however, that his formula even in its improved form (*Institutului Roman pentru Betoane*, Buletinul IV, 1936) has not been generally accepted owing to its great complications.

(2) Other investigators find that the bond effect is caused by processes entirely independent of shrinkage. The reason given is that concrete which has hardened under water, and in which, therefore, no shrinkage can occur, has a higher bond (Preuss, *Versuche über die Haftung zwischen Eisen und Beton*, *Armierter Beton*, 1910, No. 9). Preuss distinguishes between bond and resistance to slip, and says that they are approximately in the ratio of 1 to 16. His experiments with slit tubes clearly show the minute influence of grip. E. Probst finds that bond

decreases if smoothly polished steel bars dipped in oil are used, and assumes that bond depends on the tensile strength of the concrete. The greater the tensile strength the later the first cracks occur and the longer the bond between steel and concrete lasts (*Vorlesungen über Eisenbeton*, Berlin, 1917). A. Kleinlogel maintains that the greater bond strength of concrete cured in water is due to the influence of water on the chemical process of setting, but he does not arrive at a definite conclusion regarding the influence of the cross-sectional area of the steel bars (" Ueber das Wesen und die wahre Grösse des Verbundes zwischen Eisen und Beton "). E. Mörsch attempts to show that the adhesion of cement is the cause of bond strength (*Der Eisenbetonbau*, 5th edition, Vol. 1, Part 1, p. 95).

The results of the experiments vary considerably :

Bond strength according to Bach   .. 85 lb. per square inch.
Bond strength according to Funk   .. 2119 lb. per square inch.

(*Versuche an Plattenbalken, Armierter Beton*, 1909. No. 12.)

Decrease of bond strength if polished bars are used :

Probst ..   ..   ..   10 per cent.
Bach   43   ,,

Increase of bond strength if corroded bars are used :

Scheit and Wawrzinick ..   ..   .. 32.8 per cent.
Bach   74   ,,

(*Deutscher Ausschuss*, 1911, No. 7.)

Probst in his earlier experiments discovered an increase of bond strength when a smaller amount of gauging water was used, but in more recent experiments he finds a decrease of more than 50 per cent. in bond strength if concrete with a very small amount of gauging water is used (*Bauingenieur*, 1927, p. 595). R. Saliger notices great deviations in bond strength according to the disposition of the load.

More Recent Investigations.

These differences and contradictions have prompted investigators to look for other explanations of bond strength. It is believed that these can be found in the results of investigations into the physics and chemistry of capillarity. Some also assume that shrinkage is the true cause of bond strength and observe the processes of shrinkage with much more accurate apparatus.*

According to Lyse the influence of the percentage of cement in mortar on shrinkage is very small (if the percentage of cement is multiplied by $2\frac{1}{2}$, shrinkage is only increased by 10 per cent.), but the influence of the percentage of fine sand is greater. If coarse or well-graded aggregates are used shrinkage is smaller.

Nacken explains the bond effect as follows : In freshly gauged mortar, as in any supersaturated solution, the crystals grow and smaller pieces unite to

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* R. E. Davis, *Proc. Amer. Concrete Institute*, 1930, 26, 407.
W. A. Slater, *Proc. Internat. Assoc. Testing Mat.*, 1931, I, p. 1000.
Inge Lyse, *American Soc. Test. Mat.*, 1935, II, p. 383.
R. W. Carlson, *Proc. American Soc. Test. Mat.*, 1935, II, pp. 370–379.
Kurt Würzner, *Zement*, 1937, 17, IV, No. 24.
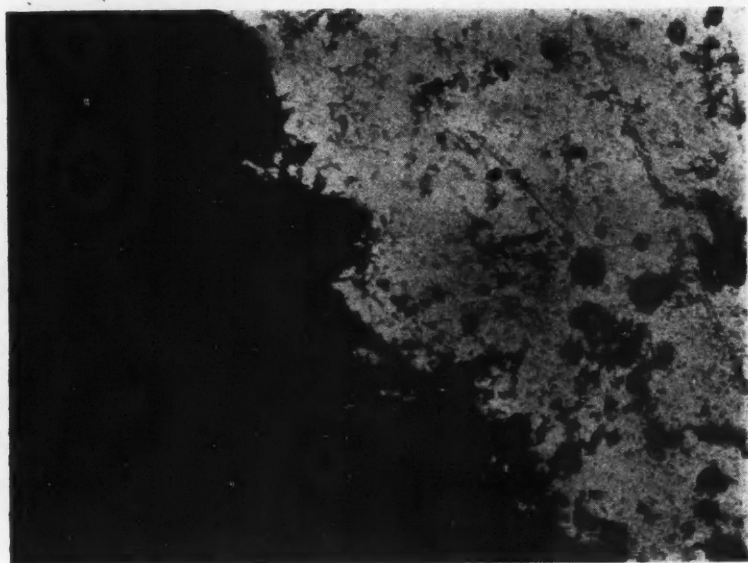R. Nacken, *Zement*, 1937, No. 43.

Fig. 1.

Fig. 2.

form greater units.   Capillary attraction brings the various units so close together that the molecules attract one another.   If the surfaces of contact are big enough great bond strength results.   Other physical processes and additional shrinkage also increase the bond.   The steel is also affected by capillary forces.   If the fine pores are filled with water, swelling sometimes occurs instead of shrinkage in cement which has set under water.

This explanation excludes all chemical processes and is based on physical phenomena alone.   Undoubtedly capillary forces have a great influence, but bond strength is not due to these forces only.   To prove this I have made special investigations, using microscopical photographs of thin slices from concrete structures.

Investigations with the Microscope.

Fig. 1 is a photograph enlarged 100 times, and *Fig.* 2 is enlarged 500 times. It can be seen from these that not only physical processes (shrinkage and capillarity) have been taking place, but that the gel and crystalline substance have filled the pores of the steel.   In some places there are even detached pieces of steel surrounded by concrete.   Thus the surface of the steel is made very rough, and consequently considerably increased.   On this greatly adhesive surface the capillary action takes place, and the cement paste and the crystals are very closely connected with the steel.

The assumption that the bond strength is directly proportional to the surface area of the steel cannot be correct.   Experiments show that the bond strength calculated from the diameter of the bars is not always equal to the true bond. The increase of bond as the diameter of the steel increases is explained by the fact that the larger bars are rolled less and therefore have a softer surface than the smaller bars.   The resistance to the attack of the newly formed crystalline material is also greater in bars of larger diameter.   Consequently, the hardness of the steel must be taken into account when calculating the bond of a given steel.

Investigations were also made of the practical applications of the experiments, and various methods of increasing the bond are suggested :

(1) Use larger bars with a softer surface and looser texture ;

(2) Soften the surface of the steel by annealing ;

(3) Roughen the surface of the steel by applying acids (the acid must afterwards be washed away) ; and

(4) Hasten the process of drying out (crystallisation) by raising the temperature at which the cement sets (avoiding quick cooling).

Temperatures and Changes of Material in the Rotary Kiln and the Lepol Kiln.

THE results of a test to determine the temperatures and changes of material in a Lepol kiln are reported by Dr. R. Koeltzsch in a recent issue of *Zement*, and are compared with Dr. Gygi's conclusions from his tests on a rotary kiln.

In the course of his thorough investigations of heating technique * Dr. Hans Gygi showed the distribution of the temperatures of the material and the
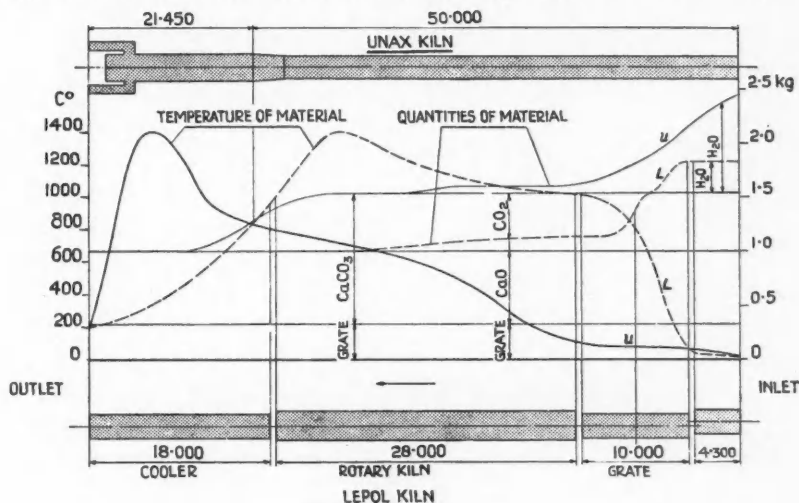

Fig. 1.

composition of the material from the raw meal to the finished clinker inside a rotary kiln. In this test the rotary kiln was about 71·45 m. long (working on the wet process) and had a diameter of 2,500 mm. in the drying and preliminary heating zones, and a diameter of 3,000 mm. in the burning zone. The kiln was equipped with a chain arrangement in the entrance zone. The rotary kiln was a Unax type with a direct-connected tube-cooler composed of twelve cooling tubes 4,450 mm. long and 1,050 mm. in diameter.

In *Fig.* 1 the curves showing the temperatures of the material and its composition are drawn above the axis of the kiln. The temperatures were measured by pyrometers consisting of a Pt.-Pt./Rh. thermo-couple for the higher temperatures and a Ni.-Ni./Cr. thermo-couple for the lower temperatures. The temperatures were taken in the different cross sections whilst the kiln was running. The distribution of the raw material components was obtained from fourteen samples taken from inside the kiln.

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* "Cement and Lime Manufacture," November and December, 1937, and February, March, April, June and July, 1938.

Experiments on a Lepol Kiln.

Without the means available to Gygi, an attempt has been made to determine the temperatures and material composition in a Lepol kiln erected in 1937, which has a similar output of about 205 tons per day and works on the dry process. It was assumed that the temperature of the material is about the same as that of the gases at the same spot. In the Lepol kiln the raw meal prepared in the granulation drum goes over the grate, through the rotary kiln itself, and the cooler, one after the other. The grate has a width of 2,300 mm. and a length of 10 m. ; the rotary kiln has a diameter of 2,800 mm. and a length of 28 m. ; the cooler is 18 m. long and has a diameter of 2,300 mm. The grate is subdivided into a drying chamber and a heating chamber. In both chambers temperatures were taken by means of a Ni.-Ni./Cr. thermocouple, and samples of material were taken from both chambers and examined. The results were :

    (1) Water-content of the nodules   ..   ..   ..   15 per cent.
    (2) Loss on ignition of nodules in the drying chamber   32 per cent.
    (3) Loss on ignition of nodules in the heating chamber   12 per cent.

From these figures the material components for 1 kg. of clinker can be estimated as follows :

	H_2O	Dry R. meal	CO_2	
Nodules	0·272	1·54	—	kg.
Ditto, drying chamber	—	1·47	0·07	,,
Ditto, heating chamber	—	1·135	0·405	,,
Clinker	—	1·0	0·540	,,

These values are also shown in the diagram above the kiln axis, and in the drawing the inlet and outlet of the kiln are made to coincide for both cases.

Conclusions.

Apart from the water-contents, which vary with the different processes, the following points emerge from a consideration of both processes.

(1) In the Lepol process the free water disappears very much earlier than in the usual rotary kiln.

(2) In the Lepol process CO_2 begins to be driven off on the grate before entering the actual kiln ; in the usual rotary kiln this only takes place in the second half of the kiln.

(3) In the Lepol kiln there is a total temperature difference of about 500 deg. C. compared with about 1,300 deg. C. in the rotary kiln.

(4) The cooling of the clinker proceeds much faster in a rotary kiln than in a Lepol kiln.

The more intense preparatory treatment of the material before entering the actual kiln of the Lepol process is most clearly shown in the diagram. The temperature rises on the grate from about 30 deg. C. to 350 deg. C. in the drying chamber and to about 1,000 deg. C. in the heating chamber. The water

of the nodules is driven off after quite a short time in the drying chamber, whilst the nodules in the heating chamber already lose 75 per cent. of their carbon dioxide on account of the high temperature, so that in the kiln itself only the balance of 0·135 kg. per kilo of clinker remains to be driven off.　On the other hand, the curves given in the diagram for the usual rotary kiln show a gentler rise of temperature till just before sintering.　The expulsion of the water goes on over the whole of the first third of the kiln whilst the exothermic reaction of clinker formation is seen only in the third section.

Measurement of Gas Temperature.

IN the course of a paper entitled " The Measurement of Gas Temperature in the Chemical Industry," delivered to a Symposium on Gas Temperature Measurement held in London in December under the auspices of the Institute of Fuel, and published in the March, 1939, number of the Journal of the Institute together with many other valuable papers read at the Symposium, Mr. J. C. Swallow dealt with the choice of pyrometers (mercury in glass, mercury in steel, thermocouples, resistance thermometers, radiation pyrometers) and their relative merits for different services.   Attention was paid to problems of measuring gas temperatures over 1200 deg. C. and to the effects of sensitivity and lag on automatic temperature control.   The subject of refractories for use with pyrometers was discussed, and also the use of metal protective sheaths.   In the course of his paper the author said the measurement of gas temperatures is necessary in the chemical industry for two distinct purposes :

(1) To control chemical plant where the changes of temperature are used to alter the variables by which the plant is controlled, either by hand or by automatic control ; and

(2) For the determination of accurate heat-transmission coefficients and heat balances of plant, the data from which may be used for future design or for the tracing of unknown heat losses.

Whilst the problems of measurement are similar in both cases, it is not, as a general rule, necessary to take the same elaborate precautions for the first, where only relative changes of temperature are of importance, whilst in the case of the second, high absolute accuracy may be very necessary.

There are no very elegant methods for the measurement of gas temperatures which are commercially applicable to chemical plant, but it would not appear that the progress of chemical engineering is seriously handicapped by this limitation.   The problems of measurement are essentially similar to those encountered in the metallurgical, refractory and gas industries.   Admittedly for purposes of control the indicated temperature of a gas is often very far from the true temperature, but represents a mean temperature which is, however, of considerable practical use.   When such temperatures are used to control a continuous plant, a much more important factor than the accuracy of the indicated temperature is the life of the thermometer under the conditions in the plant, and its ability to maintain its characteristics without deterioration.   Failure of the thermometer and the necessity for replacement may lead to stoppage of expensive plant.

It is natural, therefore, that in chemical industry more emphasis is placed on the problem of maintenance than on the obtaining of accuracy, and one of the aims of the paper is to indicate, from experience of chemical plant control, where improvements would be most helpful.

The technique employed, and the difficulties encountered, can be usefully discussed under the two headings given above.

Choice of Pyrometer.

General.—The thermometers used in practice are mercury in glass, mercury in steel, bimetallic elements which can give direct readings, thermo-elements, resistance thermometers and radiation pyrometers. For the measurement of the lowest temperatures met with in industrial practice, e.g., 190 deg. C., the resistance thermometer is the most satisfactory for accurate measurement, but for less accurate work the copper/constantan thermocouple is perfectly satisfactory and maintains its characteristics with time. Above room temperature the thermocouple appears to be the most commonly used of all thermometers in chemical plant. Iron/constantan has the advantage of cheapness and can be used up to 700 deg. C. and for occasional use up to 800 deg. C. in neutral and reducing atmospheres, and chromel/alumel is another suitable combination for this range in neutral and oxidising atmospheres up to 1,000 deg. C. Brightray-manganic can be used up to 1,000 deg. C. in neutral and oxidising atmospheres, and for occasional use up to 1,100 deg. C., but with this couple very complete protection against corrosion and gas attack is essential. All these combinations require protection against gas attack and corrosion, the degree of protection increasing rapidly with increase of temperature.

Platinum/platinum-rhodium couples are employed for continuous use up to 1,200 deg. C., but with this combination precautions against gas attack are necessary, usually involving the use of both inner refractory and an outer metal protective sheath. Where, owing to the conditions in the plant, no suitable protected combination of this type can be employed, the only alternative is to insert a wide bore sheath with closed end in the gas chamber, and measure the temperature of the end of the sheath by means of an optical or photo-electric pyrometer. A single thermocouple combination gives only a small change of electromotive force with temperature, which is normally measured by a moving coil millivoltmeter, which has the disadvantage of low sensitivity. Recording potentiometers which have been developed comparatively recently are a great improvement in this respect, and are used to an increasing extent in the control of chemical plant where close control of temperature over a narrow range of 5 deg. to 10 deg. is necessary. Resistance thermometers can be employed at higher temperatures than are commonly recommended, but where the gases are corrosive they are generally avoided on account of expense. The characteristics of a resistance thermometer made from good quality platinum are generally maintained with age to a greater extent than those of a base metal thermocouple.

Measurement of Temperature above 1,200 deg. C.—The great convenience of thermocouples as a method of temperature measurement has led to attempts to find thermoelements suitable for use at temperatures higher than those at which the couples at present available are industrially useful. Platinum/platinum-rhodium thermoelements have been used for research purposes to obtain accurate measurements of temperatures approaching the melting point of pure platinum. Under industrial conditions this is not possible, chiefly owing to the difficulty of preventing alloying of the platinum wire with silicon and with other metals

whose-oxides are easily reducible, and which have sufficiently high vapour pressures at temperatures over 1,200 deg. C. Such contamination alters the thermoelectric characteristics of the couple, and once it has occurred the readings become unreliable. The platinum-rhodium alloy is less readily contaminated than pure platinum, and couples of 5 per cent. rhodium-platinum alloy/15 per cent. rhodium-platinum alloy have been proposed.[1]

Couples of platinum-rhodium alloy/tungsten, platinum-rhodium/molybdenum, tungsten or molybdenum/graphite [2], tantalum carbide/graphite[3] and various other couples have been described, but none of these appears to be available in standardised form for installation in high-temperature chemical or metallurgical industrial plant.

In practice the advantage of the thermocouple over the resistance for the measurement of very high temperatures is illusory, since the necessity of protecting thermocouples from contamination and from accidental damage demands the use of sheaths that are impervious and robust. It is generally impossible to provide both these requirements in one sheath, owing to the nature and limitations of refractory materials. A typical protection would consist of an impervious porcelain sheath to provide the necessary gas tightness, and a heavier silicon-carbide sheath to provide the robustness and resistance to attack by furnace slags and dusts. The high thermal capacity of the total weight of material in the protective sheaths nullifies the main advantage of the thermocouple—namely, its quick response to change of temperature.

The resistance thermometer, as already pointed out, has special advantages for purposes of temperature control. It is by no means improbable that it will displace the thermocouple for high-temperature measurements, and that its use will be extended well into the range of temperatures which at the present time is almost exclusively the field of the radiation pyrometer.

Radiation pyrometers are of two main types : those which measure the total energy of the whole spectrum of the radiation emitted by the hot body or enclosure may be described as " total radiation " pyrometers ; those which measure the intensity of a monochromatic radiation are generally described as " optical " pyrometers. The latter may be further classified into those which work on the disappearing filament principle, and those which depend on cutting down the radiation arriving from the source to be measured until a match with a source of constant brightness is obtained, as typified by the Wanner pyrometer. Each of these has its special advantages.

In the various pyrometers which are at present commercially available, the total radiation type has the advantage that it can be made recording. The observations are, however, more subject to error due to departure from black-body conditions, and are in general less reliable as indicators of true temperature than

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1. Tritton & Hanson, *J. Iron & Steel Inst.*, 1924, II, 110, 94.
2. van Liempt, Rec. Trav. Chim., 1929, 585.
3. B. P. 357. 413.

observations made with the monochromatic or optical type for which corrections for departure from black-body conditions can more readily be made. It is sometimes possible to ensure black-body conditions for purposes of measurement by inserting a closed-end tube into the furnace and sighting on the closed end. The length of tube, which must be at a uniform temperature, depends to some extent on the material of the tube, but in general must be about three diameters.

Location of Thermometer.

In the control of plant in which gas temperatures are measured, it is generally possible to simplify the problem by correct location of the thermometer. For example, in a drier which is direct fired when the material to be dried is in direct contact with the hot gases, it is possible to control the degree of firing by measuring the temperature at the colder end. Often in such cases temperatures are measured which, although they are not the true temperature of the gas, represent a useful equilibrium temperature which may be the resultant of the gas temperature and the wall temperature. Large errors are also often experienced through placing the thermometer in a space where stratification of gases is occurring.

Sensitivity and Lag.

The slow response of the temperature indicator is inherent in gas-temperature measurement. The heat is conveyed to the thermometer by convection and by radiation from the walls if they are hotter than the gas, and heat is lost along the thermocouple leads by conduction, and still more along the sheath which protects it. There is also the lag due to the transfer of heat from the sheath to the thermocouple through an air gap, which inevitably exists, and the insulation round the wire. One obvious way of remedying this defect is to decrease the heat capacity of the thermometer, and consequently the conduction along the sheath, which is often only possible at the expense of the robustness of the thermometer, or to use the bare wires, but this is seldom possible because of the corrosion and contamination that inevitably occur. Thus the indicator used in practice where it is protected by a metal or refractory sheath is generally a compromise in this important respect.

A very useful method for increasing sensitivity is sometimes employed, which consists of welding the tip of the thermocouple to the bottom of the protecting metal sheath. This has been found of great value when measuring exit gas temperatures from water-gas generators where the temperature fluctuates rapidly.

Control Problems.

Lag Due to Size of Plant.—The other cause of lag in the measurement of temperature not associated with the indicator arises from the fact that, with a large chemical plant, changes in the indicator occur some considerable time after the change in conditions has been made, due to the size of the plant. Thus, a change in a flue-gas temperature, for example, may occur several minutes after the change in firing conditions. This difficulty of time lag is met with in all large chemical plants to varying extents, but is more noticeable in the case of gases where the stratification may increase the lag. Where it is necessary, therefore,

to use a change of gas temperature to control a valve, a device must be used which is often described as anticipatory, or, more scientifically, two-term, control. It has been realised for some time ([4]) that a satisfactory control should obey the general law :—

$$-\frac{dV}{dt} = k_1\theta + k_2\frac{d\theta}{dt}$$

where V is the displacement of the correcting device, and θ is the deviation of temperature from the desired value, while k_1 and k_2 are merely arbitrary constants, t being time.

Several forms of control which obey this law are now on the market, and one of them appears to be suitable for control from a thermocouple where the difficulty of amplifying the small electromotive forces produced has been overcome by converting a change in temperature to a change of pressure (Foxboro Stabilog).

The problem is similar to that of automatic control from changes of hydrogen ion concentration where the e.m.f.'s are of the same order ([5]). Satisfactory apparatus of this kind, which can be worked with a thermocouple or resistance thermometer for the control of relatively high temperatures, will probably find many uses in chemical industry. In control based on gas temperatures the " on and off " type of control is seldom of practical use, except in furnaces where the heating is mainly by radiation or where the extra heat to be controlled is a small fraction of the total heat required.

Of interest in this connection is the device which has been used successfully for several research purposes, and which might have application in special cases. In this a resistance thermometer made in the form of a spiral within a refractory tube is connected in a bridge circuit, and the stiction of the contacts of the relay is overcome by pulses from a neon lamp circuit. Temperatures of furnaces can be maintained to within a few degrees up to 1,200 deg. C. with ease.([6])   This device is now marketed in a convenient form for research and industrial purposes.([7])

Refractory Materials.

Use with Pyrometers.—Refractory materials for use with pyrometric installations may be required to serve one of three main purposes : electrical insulation both at low and high temperatures, protection of the thermocouple or resistance thermometer, or provision of a heated enclosure to serve as a " black body " in which measurements may be made with a radiation pyrometer. The properties mainly required for these three purposes are different. For the first purpose, insulation, chemical composition is all important ; for the second purpose, gas tightness and mechanical strength are primary requirements but, since the protecting sheath will in most installations be in some form of contact with the thermocouple (even if the passage of material between platinum wire and protecting tube can take place only via the vapour phase), chemical composition is also

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4. Phil. Trans. Roy. Soc. A., 1936, **235,** 415.

5. Callender & Stevenson, *J. Soc. Chem. Ind.* (Proc. Chem. Eng. Group), 1936, **18,** 108.

6. Cooke and Swallow, *J. Sci. Instr.*, 1929, **6,** 287.

7. Metropolitan-Vickers Gazette, Sept. 1936. *Engineering,* 1937, **143,** 28.

important ; for the third purpose a high degree of gas-tightness is not required, but good mechanical strength at high temperatures, and ability to withstand steep temperature gradients and sudden changes of temperature without cracking are necessary properties. Severe vibration or rough handling of thermocouples with refractory sheaths is a complication in practice, since most impermeable refractory sheaths are brittle.

Pure Oxides.—It is now possible to manufacture refractories, suitable for the various requirements of pyrometer installations, from the refractory oxides without the addition of clay. Several firms have started to manufacture refractories of pure alumina, which are at present considerably more expensive than porcelains, but their use is increasing.

For the protection and insulation of platinum wires at high temperatures, pure alumina insulators and pyrometer tubes are probably the most suitable of the various pure oxides available. Aluminium oxide has a high melting point (2,050 deg.), good electrical properties at high temperatures, and good mechanical properties at temperatures up to 1,700 deg. C. The coefficient of thermal expansion is approximately $1\frac{1}{2}$ to 2 times that of porcelain, but the material has a high thermal conductivity and reasonably good resistance to thermal shock. Pyrometer tubes can be made which are completely gas tight at room temperatures, and at high temperatures are as impervious as the best refractory porcelains. Such tubes are, moreover, free from the irritating tendency to deteriorate rapidly due to recrystallisation at quite moderate temperatures, and are free from those constituents of ordinary porcelain tubes which give rise to the contamination of platinum wires.

It is apparent that the use of alumina as refractory may be expected to increase very greatly both the life and the useful range of platinum resistance thermometers and thermocouples.

Porcelains.—The term porcelain covers a wide variety of compositions.

				1 Marquardt	2 An English Porcelain	3 Pythagoras	4 Ordinary Porcelain
SiO_2	..	..	..	35·12	32·36	40·08	71·6
Al_2O_3	..	..	..	63·20	61·12	52·97	24·7
Fe_2O_3	..	..	..	—	0·70	0·85	—
TiO_2s	..	..	..	—	2·10	0·30	—
CaO	..	..	..	—	1·12	0·84	—
MgO	..	..	..	—	0·35	0·72	—
Ma_2O	..	..	..	—	1·02	1·07	—
K_2O	..	..	..	1·65	1·77	2·42	3·25

The following compositions are typical of the best porcelains : (1) Analysis of Marquardt porcelain given by W. L. Hewart. (2) High quality porcelain made by a reputable English firm. (3) Pythagoras porcelain, by Messrs. Haldenwanger of Berlin. (4) Ordinary porcelain, F. H. Riddle's No. 1 body. The first three of these porcelains would be manufactured from mixtures of clays with additions of alumina and felspar. No. 4, an ordinary " Hard Paste " or electrical porcelain, would be made from a mixture of clays with additions of silica and felspar. The

analysis given does not include the minor constituents TiO_2, Fe_2O_3, etc., which would be present in small amounts as impurities in the clays.

The user of porcelain tubes is perhaps less interested in the raw materials than in the composition of the finished product. A complete examination of pythagoras by chemical and microscopic means has shown it to consist entirely of mullite (a crystalline material having the composition $3Al_2O_3.2SiO_2$) and glass. A certain amount of mullite would be dissolved in the glass, and the relative proportions will depend on the heat treatment which the sample has received. Porcelains of the type of No. 4 would also be liable to contain a certain amount of undissolved silica which, present usually as cristobalite and probably tridymite, imposes its peculiar expansion characteristics on the mass in some degree. Such porcelains are in general unsuitable for use at temperatures above 1,000 deg. C. Whilst porcelains with higher alumina content are more refractory than the ordinary high silica porcelains, the temperature at which they can be used as sheaths is still limited by the attack of the material on the thermocouple or platinum resistance thermometers.

Corrosion of Metal Sheaths.

The properties of fused silica are well known and need no more than passing reference. The chemical composition of fused silica (pure SiO_2) renders it unsuitable for use in conjunction with platinum pyrometers at high temperature. The material undergoes recrystallisation when heated continuously above 1,000 deg. C. Tubes which have so recrystallised, however, remain intact for long periods if not cooled, and for this reason fused silica finds application as a material for sight tubes in many radiation pyrometer installations. Where the gases are very corrosive and a gas-tight sheath is required, it is necessary to use heat-resisting metal.

Apart from the harmful action which can be exerted on special steels by gases containing sulphur compounds and steam, consideration must first be given to the " free scaling " temperature under normal oxidising conditions. Mild steel begins to scale appreciably at temperatures over 600 deg. C., and for prolonged service above such a temperature the use of alloy steels is necessary.

Good heat resistance is shown by chromium and chromium-nickel steels, and the ordinary $18/8/1/1$ (tungsten, titanium)* shows good resistance to oxidising conditions up to 900 to 950 deg. C. ; further improvement is obtained by addition of silicon and by increasing the tungsten up to 4 per cent.

Where fuels containing 1 to 2 per cent. sulphur are being burnt, it is advisable to change over to the straight high chromium steels containing 30 per cent. Cr ; the maximum temperature at which such materials can be used is raised to 1,100 deg. C., by the addition of aluminium—the formation of a complex chromium-aluminium oxide skin exerting a protective action.

The oxidising action of hot gases on the special steels may be accelerated by the presence of small amounts of substances such as lead oxide, sodium compounds, copper oxide, etc., which may exert a fluxing action on the oxide film.

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* 18% Cr, 8% Ni, 1% W, 1% Ti.

The use of aluminium-iron alloys on the surface of the metal as obtained in processes such as calorising, is possible for temperatures up to 950 deg. C., and such coatings are resistant to sulphur-bearing gases.   The straight iron-aluminium alloys, with and without small amounts of chromium (Feralloy) if they can be cast free from the skin and oxide defects give good resistance up to 1,050 deg. C.

Absorption of carbon by iron-chromium and iron-nickel-chromium alloys in carburising atmospheres may cause serious embrittlement ; this can be ameliorated by using low iron content nickel-chromium alloys of the 80/20 type, an example of which is " Cronite."

The affinity of chromium for nitrogen may also give rise to embrittlement in the synthesis of ammonia at high temperatures and in nitriding operations, where the use of alloys of high nickel content may be useful.

The action of hydrogen under pressure at elevated temperatures can be very destructive ; the subject has been fully dealt with elsewhere.[8]

The average thermocouple sheath can be made up either as a casting, in which case a comparatively thick wall is usually necessary, or it can be made by welding an end on to a solid drawn steel tube.   Many of the alloys mentioned in this note can only be obtained as castings—tubes of the 25/20 and 18/8 chromium-nickel steels can be obtained, but care should be taken to see that such steels are of a suitable composition for welding, i.e., that they are not susceptible to the well-known disintegration phenomena common to these steels ; additions of titanium, silicon or niobium are necessary to prevent this.

Contamination of Thermocouples.

Detection.—The contamination of thermocouples as used in practice may be due to corrosion by the gases or to permeability of the metal of refractory sheaths. A useful method of determining whether contamination has taken place when consistent errors are experienced consists of stretching the wire between two water-cooled clamps.   A small flat coal-gas flame mounted on a moving carriage is then arranged to traverse the length of the wire, the ends of the wire being connected to a galvanometer.   If the wire is contaminated, the steep temperature gradient in a small length of the wire causes a small current to flow.

Readings are taken over the whole length of the wire, moving the flame 1 in. or $\frac{1}{2}$ in. at a time until the contamination is detected.   Such a simple installation is of great help in determining whether contamination of thermoelements is taking place in chemical plant.

Calibration.

Where a large number of thermocouples are used in chemical plant, it is often of great advantage to be in a position to calibrate against, say, a standard resistance thermometer.   To immerse the thermometers to be checked in an air thermostat can lead to quite large errors due to the uneven distribution of temperature. It is more satisfactory to have a bath of molten salts, consisting of an equimole-

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8. Inglis and Andrews, *J. Iron & Steel Inst.*, 1933, II, **128,** 383.

cular mixture of potassium and sodium nitrates which is stirred, in which all the thermometers can be immersed. Such an arrangement is very convenient for temperatures up to 500 deg. C., where the temperature can be easily varied and is to be preferred to the tedious calibrations at the fixed temperatures of the boiling point of water and sulphur. For calibration at higher temperatures of standard thermocouples, the melting points of gold and palladium can be used.

Special Problems.

Under this heading problems are met where true gas temperatures are required, and which necessitate the use of special apparatus.

Radiation.—A most difficult problem is to eliminate the effect of radiation on the thermometer. Whilst in theory this difficulty can be overcome by insulated walls, in practice this is not feasible. The only satisfactory way of eliminating this error is by using a " sucking " or high-velocity thermocouple in which the thermocouple itself is encased in a reflecting protecting tube, and the gases are sucked past the thermocouple at a high velocity. A number of satisfactory devices of this sort has been described in the literature, [9] and provided sufficient precautions are taken, true " gas temperatures " can be measured up to 1,200 deg. or 1,300 deg. C. In normal chemical engineering practice, however, such devices scarcely justify the complication to provide the extra accuracy. Such a device is, however, preferable to the determination of temperature by thermocouples with wires of varying thickness, and extrapolating to the value for wires of negligible thickness.

Whilst the reading obtained with a thermocouple of very fine wire is often very close to the value obtained with the " high-velocity " thermocouple, it must be remembered that the former can only be used for a very short time in a contaminating gas.

High Pressure.—Another problem which is becoming more important is the measurement of gas temperatures in high-pressure vessels where an exothermic chemical reaction is taking place with dissipation of heat through the walls. The sheath of the thermocouple must be capable of withstanding the pressure in the vessel, and in consequence is generally so thick that conduction along it is excessive, and the temperature measured is intermediate between that of the gas and the walls of the vessel. In such cases where true gas temperatures are required, it is sometimes necessary to introduce the bare wires of the thermocouple through electrically insulated pressure-tight joints. Of interest in this connection is a method by which the leads can be taken into the vessel through glass insulators which are sealed into a high chromium steel.[10] This has been satisfactorily used for research purposes, but should be equally well applicable to chemical plant.[11]

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